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# Asymptotic correction of the exchange–correlation kernel of time-dependent density functional theory for long-range charge-transfer excitations

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Time-dependent density functional theory (TDDFT) calculations of charge-transfer excitation energies $\omega_{CT}$ are significantly in error when the adiabatic local density approximation (ALDA) is employed for the exchange–correlation kernel $f_{xc}$. We relate the error to the physical meaning of the orbital energy of the Kohn–Sham lowest unoccupied molecular orbital (LUMO). The LUMO orbital energy in Kohn–Sham DFT—in contrast to the Hartree–Fock model—approximates an excited electron, which is correct for excitations in compact molecules. In CT transitions the energy of the LUMO of the acceptor molecule should instead describe an added electron, i.e., approximate the electron affinity. To obtain a contribution that compensates for the difference, a specific divergence of $f_{xc}$ is required in rigorous TDDFT, and a suitable asymptotically correct form of the kernel $f_{xc}^{asymp}$ is proposed. The importance of the asymptotic correction of $f_{xc}$ is demonstrated with the calculation of $\omega_{CT}(R)$ for the prototype diatomic system HeBe at various separations $R$(He–Be). The TDDFT–ALDA curve $\omega_{CT}(R)$ roughly resembles the benchmark *ab initio* curve $\omega_{CT}^{CISD}(R)$ of a configuration interaction calculation with single and double excitations in the region $R=1-1.5$ Å, where a sizable He–Be interaction exists, but exhibits the wrong behavior $\omega_{CT}(R) \ll \omega_{CT}^{CISD}(R)$ at large $R$. The TDDFT curve obtained with $f_{xc}^{asymp}$ however approaches $\omega_{CT}^{CISD}(R)$ closely in the region $R=3-10$ Å. Then, the adequate rigorous TDDFT approach should interpolate between the LDA/GGA ALDA xc kernel for excitations in compact systems and $f_{xc}^{asymp}$ for weakly interacting fragments and suitable interpolation expressions are considered. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1759320]

## I. INTRODUCTION

One of the problems of time-dependent density functional theory (TDDFT) remains the systematic underestimation of excitation energies $\omega_{CT}$ associated with molecular long-range charge transfer (CT) between an electron donor ($D$) and electron acceptor ($A$).[1–3] This erroneous behavior stands in marked contrast to the success of TDDFT in calculations of excitations in compact molecules and of intrafragmental excitations in larger systems. This success of TDDFT is based on the efficient calculation of excitation energies $\omega_k$ as eigenvalues of the following eigenvalue problem:[4]

$$[\boldsymbol{\mathcal{E}}^2+2\boldsymbol{\mathcal{E}}^{1/2}\mathbf{K}\boldsymbol{\mathcal{E}}^{1/2}]\mathbf{F}_k=\omega_k^2\mathbf{F}_k. \tag{1}$$

In (1) $\boldsymbol{\mathcal{E}}$ is the diagonal matrix containing the orbital energy differences

$$\boldsymbol{\mathcal{E}}_{ib,jc}=(\varepsilon_b-\varepsilon_i)\,\delta_{ij}\delta_{bc} \tag{2}$$

of virtual KS orbitals $\phi_b$ and occupied orbitals $\phi_i$, and $\mathbf{K}$ is the so-called coupling matrix (we consider real orbitals and singlet–singlet excitations)

$$K_{ib,jc}=\int d\mathbf{r}_1\int d\mathbf{r}_2\,\phi_i(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\times\left[\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}+f_{xc}(\mathbf{r}_1,\mathbf{r}_2,\omega)\right]\phi_j(\mathbf{r}_2)\phi_c(\mathbf{r}_2). \tag{3}$$

The exchange–correlation (xc) kernel $f_{xc}$ is the functional derivative of $E_{xc}$ with respect to the time-dependent ground state density $\rho(\mathbf{r},t)$,

$$f_{xc}(\mathbf{r}_1,\mathbf{r}_2,t_1,t_2)=\frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r}_1,t_1)\,\delta\rho(\mathbf{r}_2,t_2)}=\frac{\delta\nu_{xc}([\rho];\mathbf{r}_1,t_1)}{\delta\rho(\mathbf{r}_2,t_2)}, \tag{4}$$

where $E_{xc}[\rho]$ is the ground state xc energy functional and $\nu_{xc}$ is the ground state xc potential. In systems where transitions take place between orbitals in the same spatial region, already the zero-order TDDFT, the orbital energy differences (2) provide a fair estimate of excitation energies $\omega_k$ and the coupling terms in (1) often improve it further even with a simple adiabatic local density approximation (ALDA) for $f_{xc}$.

However, the ALDA $f_{xc}$ used routinely in TDDFT leads to a systematic underestimation of the excitation energy $\omega_{CT}$ of a CT transition between distant donor $D$ and acceptor $A$ molecular fragments. This problem has been highlighted in Refs. 1–3. In Ref. 2 a hybrid approach of TDDFT and the configuration interaction singles (CIS) method[5] has been employed for this problem, and in Ref. 3 the hybrid approach has been applied to calculation of $\omega_{CT}$ for realistic CT complexes.

 

In this paper it is shown that the problem of long-range charge-transfer excitations can be resolved within a pure DFT framework. In Sec. II this problem is related to a fundamental feature of Kohn–Sham (KS) theory, the essentially positive difference $\Delta^A=\varepsilon_a^- - \varepsilon_a$ between the energy $\varepsilon_a^-$ of the highest occupied orbital $\phi_a$ of the anionic acceptor fragment $A^-$, containing the "extra" electron, and the orbital energy $\varepsilon_a$ of the LUMO of the neutral *A*. A "frozen orbital" DFT estimate of $\Delta^A$ is considered. The difference $\Delta^A$ is evaluated from accurate molecular KS solutions for the small prototype molecules CO, $N_2$, $H_2O$, HF, HCl, HCN and it appears to be rather large. In Sec. III $\Delta^A$ is incorporated into the TDDFT description of CT. This requires a specific divergence of the exchange–correlation (xc) kernel $f_{\rm xc}$ and of the corresponding response $\delta\nu_{\rm xc}$ of the xc potential. An asymptotically correct form $f_{\rm xc}^{\rm asymp}$ of the xc kernel is derived, which provides the required correction to $\omega_{\rm CT}$ calculated with TDDFT. Conditions for switching on $f_{\rm xc}^{\rm asymp}$ are established. In Sec. IV the $\omega_{\rm CT}$ values obtained with $f_{\rm xc}^{\rm asymp}$ for CT transitions $1s({\rm He})\rightarrow 2p_\pi({\rm Be})$ in the prototype diatomic system HeBe, for various He–Be separations $R$(He–Be), are compared with those calculated with the CI singles and doubles (CISD) method as well as with the combination of the approximation of statistical averaging of (model) orbital potentials (SAOP)[6] for $\nu_{\rm xc}$ and the ALDA $f_{\rm xc}$. The CISD yields a curve $\omega_{\rm CT}(R)$ with a minimum at $R=2.5$ Ångstrom and increasing at larger $R$(He–Be) correctly to the difference between the ionization energy of the donor and the electron affinity of the acceptor. The TDDFT excitation energy $\omega_{\rm CT}$ calculated with the ALDA $f_{\rm xc}$ decreases with *R*, approaching rather rapidly a much too low asymptotical value (equal to the KS orbital energy difference $\varepsilon_a-\varepsilon_d$ between the LUMO of the acceptor and the HOMO of the donor). Contrary to this, $f_{\rm xc}^{\rm asymp}$ reproduces the increase of $\omega_{\rm CT}$ with *R* in good agreement with the curve obtained with CISD. In Sec. V the conclusions are drawn and the implications of the presented results for TDDFT are made.

## II. ORIGIN OF THE LONG-RANGE CT PROBLEM IN TDDFT

The long-range CT problem of TDDFT is related to a fundamental feature of Kohn–Sham (KS) theory, the essentially positive difference $\Delta^A=\varepsilon_a^- - \varepsilon_a$ between the energy $\varepsilon_a^-$ of the "extra" electron in the highest occupied orbital $\phi_a$ of the anionic acceptor fragment $A^-$ and the orbital energy $\varepsilon_a$ of the LUMO of the neutral *A* (see Fig. 1). The KS orbital energies of the highest occupied orbitals are strictly equal to vertical ionization potentials (VIP), so for the donor $\varepsilon_d=-I^D$, and for the acceptor $\varepsilon_{a-1}=-I^A$, and for $A^-$ we must have $\varepsilon_a^-=-I^{A^-}=-A^A$, where $A^A$ is the electron affinity (EA) of *A*. It is well known that on the other hand the LUMO orbital energy of neutral *A*, $\varepsilon_a$, does not correspond to the electron affinity. It is a basic feature of the KS solution of an *N* electron system that all occupied orbitals ($\varphi_i$) and virtual orbitals ($\varphi_b$) are obtained with the same local, state-independent KS potential $\nu_s(\mathbf{r}_1)$, so that they all "feel" the effective field of $N-1$ electrons. Because of this, the energies of the KS virtual orbitals represent an "excited" electron interacting with $N-1$ electrons, rather than an "extra" electron interacting with *N* electrons. This is a large and important difference with Hartree–Fock, where the LUMO orbital energy represents approximately the energy of an added electron (in the field of all other *N* electrons), and therefore is physically more like an electron affinity than like an energy of an excited electron. Kohn–Sham orbital energy differences are therefore much better approximations to vertical excitation energies than Hartree–Fock orbital energy differences are, at least for excitations in compact molecules or for intrafragmental excitations in larger systems.

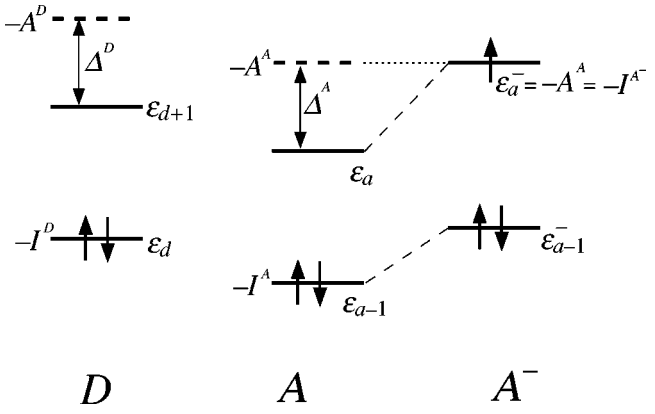


FIG. 1. Schematic illustration of the positions of the exact Kohn–Sham orbital energies in relation to the ionization energies and electron affinities of the neutral donor (*D*) and acceptor (*A*) systems and of the negative $A^-$. The magnitude of the gap $\Delta$ between LUMO energy and electron affinity $-A$ is indicated for *D* and *A*, as well as the equality of $-A^A$ and $\varepsilon_a^-$.

On the other hand, with a weak donor (*D*)–acceptor (*A*) interfragment interaction at the large $D-A$ separation *R* the true CT excitation energy $\omega_{\rm CT}$ becomes the difference between the vertical ionization potential $I^D$ of the donor and the electron affinity $A^A$ of the acceptor corrected with the electron–hole interaction $-1/R$,

$$\omega_{\rm CT}\approx I^D - A^A - 1/R. \tag{5}$$

At large separations *R* the difference $(I^D-A^A)$ becomes the dominant term of (5). However, as was pointed out in Ref. 2, at large separations *R* the TDDFT calculations will give zero contribution from the coupling matrix, because the transition density $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ becomes identically zero, i.e., the TDDFT calculation reduces to the zero-order result (2), $\varepsilon_a^- - \varepsilon_a$. It is evident that the error is $\Delta^A$,

$$\begin{aligned}\omega_{\rm CT}-\omega_{\rm CT}^{\rm TDDFT(0)} &\approx I^D - A^A - (\varepsilon_a-\varepsilon_d)\\ &= \varepsilon_a^- - \varepsilon_a = \Delta^A\\ &= \langle \phi_a^- | \hat{T} + \nu_s(N+1) | \phi_a^- \rangle\\ &\quad - \langle \phi_a | \hat{T} + \nu_s(N) | \phi_a \rangle. \end{aligned}\tag{6}$$

Physically this means that when the excited electron is not "landing" in a virtual orbital on the same molecule (or fragment) where also the hole is that it leaves behind, but on a remote fragment, it is not correct that it goes into a level that is essentially stabilized by the attraction to a hole ($\varepsilon_a$), but it should go to an affinity level ($\varepsilon_a^-$). The quantity $\Delta^A$ is just the destabilization of the *a* level from *A* to $A^-$, $\Delta^A$

TABLE I. The difference $\Delta_a$ (in eV) between the energies of "extra" and "excited" electrons for the molecular Kohn–Sham solution, $\Delta_1^A$ is estimated from the negative electron affinities of Refs. 8 and 9 as $\Delta_1^A=-\varepsilon_a-A^A$, while $\Delta_2^A=-\varepsilon_a$.

| Molecule | CO | $N_2$ | $H_2O$ | HF | HCl | HCN |
|---|---|---|---|---|---|---|
| $\Delta_1^A$ | 8.36 | 8.98 | 8.05 | 9.58 | 8.66 | 7.28 |
| $\Delta_2^A$ | 6.56 | 6.77 | 5.11 | 5.71 | 5.36 | 5.53 |

$=\langle\phi_a^-|\hat{T}+\nu_s(N+1)|\phi_a^-\rangle-\langle\phi_a|\hat{T}+\nu_s(N)|\phi_a\rangle$. Making the somewhat drastic approximation $\phi_a^-\approx\phi_a$, we obtain for the destabilization $\Delta^A$ approximately

$$\Delta^A\approx\langle\phi_a|\nu_{\mathrm{Coul}}(|\phi_a|^2)+\nu_{\mathrm{xc}}(\rho^A+|\phi_a|^2)-\nu_{\mathrm{xc}}(\rho^A)|\phi_a\rangle$$
$$=K_{aa,aa}^{\mathrm{Coul}}+\langle\phi_a|\nu_{\mathrm{xc}}(\rho^A+|\phi_a|^2)-\nu_{\mathrm{xc}}(\rho^A)|\phi_a\rangle, \quad (7)$$

where $K_{ij,kl}^{\mathrm{Coul}}$ is the two-electron integral $\int d\mathbf{r}_1\int d\mathbf{r}_2\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2)/|\mathbf{r}_1-\mathbf{r}_2|$. We note that $\Delta^A$ is often called the derivative discontinuity. This originates from the analysis in Ref. 7 which showed that when we want to use the single Kohn–Sham system with fractional number of electrons $N+\delta$ ($\delta$ electrons in $\phi_a$) to represent the density of an ensemble of the exact $N$-electron and $(N+1)$-electron systems, the orbital $\phi_a$ must have the orbital energy $\varepsilon_a^-$ in order to reproduce the proper asymptotic decay of the density. The KS potential $\nu_{\mathrm{xc}}$ of the constructed KS system must therefore exhibit the shift $\Delta^A$ at the $\delta=0$ point, i.e., $\lim(\delta\downarrow 0)\langle\phi_a|\nu_{\mathrm{xc}}(N+\delta)-\nu_{\mathrm{xc}}(N)|\phi_a\rangle=\varepsilon_a^--\varepsilon_a=\Delta^A$. This result however does not enable us to obtain a physical prescription to calculate $\Delta^A$, and it will not play a role in the context of the present paper.

Table I presents for the small prototype molecules CO, $N_2$, $H_2O$, HF, HCl, HCN the values $\Delta_1^A$ which are evaluated using the electron affinities $A^A$ reported in Refs. 8 and 9 and the LUMO energies $\varepsilon_a$ of the rather accurate ("exact") molecular KS solutions obtained in Ref. 10. The "exact" KS solutions are obtained with KS potentials which are generated from *ab initio* (CISD[11,12]) electron densities $\rho$ with the iterative local updating procedure of van Leeuwen and Baerends (LB)[13] (see for the LB procedure also Ref. 14). The $A^A$ values have been obtained theoretically in Refs. 8 and 9, and are in fact negative for all of the small molecules considered here, but they tend to decrease for larger basis sets used.[9] Having in mind this tendency and anticipating that in the considered molecules an extra electron should occupy a weakly bound level, we also present in Table I the values of $\Delta^A$ estimated with $\varepsilon_a^-\approx 0$, i.e., $\Delta_2^A\approx-\varepsilon_a$.

For the systems considered, the evaluated $\Delta^A$ is rather large in both variants $\Delta_1^A$ and $\Delta_2^A$, varying from 7.28 eV for HCN to 9.58 eV for HF in the case of $\Delta_1^A$ and from 5.11 eV for $H_2O$ to 6.77 eV for $N_2$ in the case of $\Delta_2^A$. According to (6), this will lead to a large underestimation of the excitation energy $\varepsilon_a-\varepsilon_d=\omega_{\mathrm{CT}}^{\mathrm{TDDFT}(0)}$ with the zero-order TDDFT. And the standard adiabatic approximations (either LDA or GGA) for $f_{\mathrm{xc}}$ do not lead to any correction from the full TDDFT calculation including the coupling matrix (3).[2] The large underestimation of the CT excitation energy is a result of the lack of this coupling matrix contribution, not by any "deficiency" of the KS orbital energies, whose physical meaning is clear. It is not improved when GGA approximations to the orbital energies are used, since both the HOMO orbital energy of system $D$ and the LUMO orbital energy of system $A$ are shifted upwards compared to the exact Kohn–Sham values. (These upshifts have been estimated to be approximately $\Delta^D/2$ and $\Delta^A/2$, respectively,[15] but rather large deviations from this estimate are known to occur occasionally.[14]) It will also not be improved when we use a KS potential like SAOP, which approximates the exact KS orbital energies more closely.

## III. AN ASYMPTOTICALLY CORRECT xc KERNEL

In the rigorous TDDFT which, in principle, should reproduce true single electron excitation energies, the zero-order error for CT excitation energies is to be fixed with the second term in the left-hand side of (1) with the coupling matrix (3). In order to get a simple TDDFT estimate $\omega_{\mathrm{CT}}^{\mathrm{TDDFT}}$, we assume that the $D\rightarrow A$ CT is associated with a single orbital excitation $\phi_d\rightarrow\phi_a$ from the highest occupied molecular orbital (HOMO) $\phi_d$ localized on $D$ to the lowest unoccupied MO (LUMO) $\phi_a$ localized on $A$, so that one can neglect the admixture in (1) of other single orbital excitations. This yields the following expression for $\omega_{\mathrm{CT}}^{\mathrm{TDDFT}}$:

$$(\omega_{\mathrm{CT}}^{\mathrm{TDDFT}})^2=(\varepsilon_a-\varepsilon_d)^2+2(\varepsilon_a-\varepsilon_d)\times\int d\mathbf{r}_1\int d\mathbf{r}_2\,\phi_d(\mathbf{r}_1)\phi_a(\mathbf{r}_1)\times\left[\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}+f_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2,\omega)\right]\phi_d(\mathbf{r}_2)\phi_a(\mathbf{r}_2). \quad (8)$$

As was pointed out in Ref. 2, for large $D-A$ separations there will be practically zero differential overlap between $\phi_d(\mathbf{r})$ and $\phi_a(\mathbf{r})$, i.e., the transition density $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ will be virtually identically zero. In this case the matrix element $K_{da,da}$ will vanish for the standard ALDA as well as for other currently employed approximations for $f_{\mathrm{xc}}$. But this means, that the calculated value $\omega_{\mathrm{CT}}^{\mathrm{TDDFT}}$ is close to the zero-order estimate, $\omega_{\mathrm{CT}}^{\mathrm{TDDFT}}\approx\omega_{\mathrm{CT}}^{\mathrm{TDDFT}(0)}=\varepsilon_a-\varepsilon_d$ for the adiabatic LDA and GGA approximations to $f_{\mathrm{xc}}$ when the differential overlap $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ becomes zero. Thus, TDDFT calculations with the standard approximations will lead to the large underestimation of the CT excitation energy mentioned in the preceding section (see also the next section for a numerical example).

In order to reproduce the true $\omega_{\mathrm{CT}}$ of (6), the rigorous $f_{\mathrm{xc}}$ should guarantee for the case of vanishing zero differential overlap $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ the positive finiteness of its matrix element $K_{da,da}^{\mathrm{xc}}=\int d\mathbf{r}_1\int d\mathbf{r}_2\phi_d(\mathbf{r}_1)\phi_a(\mathbf{r}_1)f_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2,\omega)\phi_d(\mathbf{r}_2)\phi_a(\mathbf{r}_2)$ as well as the positive finiteness of the matrix element of the corresponding change of the xc potential $\delta\nu_{\mathrm{xc},da}=K_{da,da}^{\mathrm{xc}}\delta P_{da}(\omega)$, where $\delta P_{da}(\omega)$ is the change of the density matrix associated with the CT. This requires the divergence of $f_{\mathrm{xc}}(\omega)$ and $\delta\nu_{\mathrm{xc}}(\omega)$, at least at the resonance frequency $\omega=\omega_{\mathrm{CT}}$.

The asymptotics (at large $R$) of $f_{\rm xc}$, which is required to produce the correct $\omega_{\rm CT}$, can be derived from (5) and (8) in the following form:

$$f_{\rm xc}^{\rm asymp}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\frac{\exp(-K_{da,da}^{\rm Coul}/K)^2}{K_{da,da}^{\rm Coul}} \times\left[\Delta^A-K_{da,aa}^{\rm Coul}+\frac{(\Delta^A-K_{dd,aa}^{\rm Coul})^2}{2(\varepsilon_a-\varepsilon_d)}\right]. \quad (9)$$

The exponent in (9) with the empirical parameter $K\ll 1$ guarantees, that in practical applications the asymptotics (9) will be ''switched on'' only in the case of near-zero differential overlap $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ considered above, in which case $K_{da,da}^{\rm Coul}\to 0$ and $\exp(-K_{da,da}^{\rm Coul}/K)^2\sim 1$. With this, when inserted in (8), $f_{\rm xc}^{\rm asymp}$ of (9) yields the corrected $\omega_{\rm CT}^{\rm TDDFT}$,

$$\omega_{\rm CT}^{\rm TDDFT}=\varepsilon_a-\varepsilon_d+\Delta^A-K_{dd,aa}^{\rm Coul}. \quad (10)$$

As follows from the previous discussion, (10) reproduces the true excitation energy of (5), with $K_{dd,aa}^{\rm Coul}$ in (10) being close to $-1/R$ at large $R$. The stabilization by the remote hole with respect to the energy $\varepsilon_a^-=\varepsilon_a+\Delta^A$ is only $-K_{dd,aa}^{\rm Coul}\approx -1/R$, and the switching function $\exp(-K_{da,da}^{\rm Coul}/K)^2$ in (9) should take care of the smooth transition of the stabilization with respect to the affinity $\varepsilon_a^-=\varepsilon_a+\Delta^A$ from on the one hand $-\Delta^A$ (i.e., to $\varepsilon_a$) for a local excitation, by the hole on the same fragment, to on the other hand $-K_{dd,aa}^{\rm Coul}$ by the hole on the other fragment in a CT transition. The latter becomes increasingly less significant with increasing $R$. In particular, the asymptotics (9) should be switched on in the region where the hole–particle interaction $-K_{dd,aa}^{\rm Coul}$ no longer provides an approximate cancellation of $\Delta^A$, i.e., when the difference $(\Delta^A-K_{dd,aa}^{\rm Coul})$ becomes significantly positive. The precise form of the switching can be further fine-tuned.

Due to the vanishing integral $K_{da,da}^{\rm Coul}$ in the denominator, (9) diverges when $\phi_d$ and $\phi_a$ are localized on the distant fragments $D$ and $A$, respectively. The corresponding change of the xc potential

$$\delta\nu_{\rm xc}(\mathbf{r}_1)=\delta P_{da}(\omega)\int d\mathbf{r}_2\, f_{\rm xc}^{\rm asymp}(\mathbf{r}_1,\mathbf{r}_2)\phi_d(\mathbf{r}_2)\phi_a(\mathbf{r}_2) = \frac{\exp(-K_{da,da}^{\rm Coul}/K)^2}{K_{da,da}^{\rm Coul}}\left[\Delta^A-K_{dd,aa}^{\rm Coul} + \frac{(\Delta^A-K_{dd,aa}^{\rm Coul})^2}{2(\varepsilon_a-\varepsilon_d)}\right]\delta P_{da}(\omega)\int d\mathbf{r}_2\frac{\phi_d(\mathbf{r}_2)\phi_a(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \quad (11)$$

also diverges, at least at the resonance $\omega=\omega_{\rm CT}$, for which $\delta P_{da}(\omega)$ is not small.

## IV. CT EXCITATION IN HeBe

In order to assess the effect of $f_{\rm xc}^{\rm asymp}$ of (9), $\omega_{\rm CT}$ has been calculated for the prototype diatomic system HeBe at various separations $R$(He–Be). We consider the CT excitation, which is associated with an electron transfer from the $1s$ HOAO of the He atom to the $2p_\pi$ LUAO of the Be atom. The reference $\omega_{\rm CT}^{\rm CISD}$ values have been obtained with CISD calculations performed with the ATMOL package[11] in the augmented correlation-consistent polarized core-valence 5-zeta (aug-cc-pCV5Z) basis[16] with all $f$ and $g$ functions excluded. The Davidson diagonalization procedure[17] has been employed within the ATMOL package to obtain $\omega_{\rm CT}^{\rm CISD}$. In Fig. 2 the calculated CISD curve $\omega_{\rm CT}^{\rm CISD}(R)$ is compared with the TDDFT one $\omega_{\rm CT}^{\rm SAOP-ALDA}(R)$ obtained with the combination of the approximation of statistical averaging of (model) orbital potentials (SAOP)[6] for $\nu_{\rm xc}$ and the ALDA $f_{\rm xc}$ within the ADF–RESPONSE package.[18] The SAOP xc potential $\nu_{\rm xc}^{\rm SAOP}$ has the correct long-range Coulombic asymptotics, $\nu_{\rm xc}^{\rm SAOP}(\mathbf{r}_1)\to -1/|\mathbf{r}_1|$ at $|\mathbf{r}_1|\to\infty$ (Ref. 19) and for prototype small molecules it reproduces rather well the energies of outer valence KS orbitals,[20] although we will see that for the $1s$ of He it happens to make a rather large error.

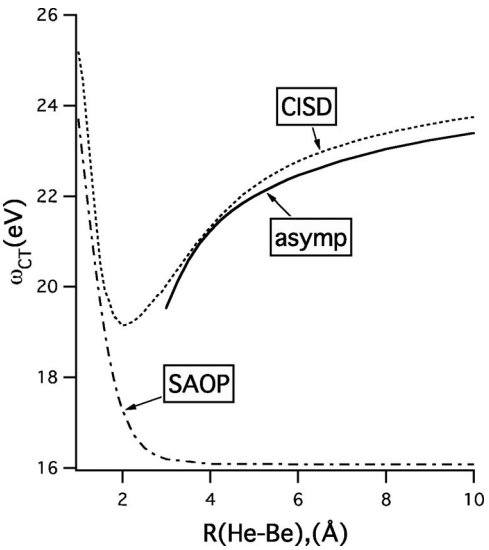


FIG. 2. The CT excitation energy $\omega_{\rm CT}$ as a function of $R$(He–Be) calculated with SDCI, SAOP–ALDA, and with $f_{\rm xc}^{\rm asymp}$.

In order to calculate $\omega_{\rm CT}$ at larger $R$ with $f_{\rm xc}^{\rm asymp}$ via (8) and (9), the required integrals $K_{da,da}^{\rm Coul}$, $K_{dd,aa}^{\rm Coul}$ are extracted from the rather accurate KS solution obtained for HeBe with the iterative LB procedure[13,14] from the CISD electron density $\rho$. In Ref. 9 a relatively small negative value $A^{\rm Be}=-0.232$ eV has been reported for Be. With this, the curve $\omega_{\rm CT}^{\rm asymp}(R)$ is obtained with the asymptotically correct energies $\varepsilon_d=-I^{\rm He}=-24.59$ eV and $\varepsilon_a=-5.95$ eV, the latter energy being taken from the accurate KS solution for the Be atom, and the $\Delta_1^A$-type estimate for $\Delta^A$, $\Delta^{\rm Be}\approx-\varepsilon_a+0.23=6.18$ eV. $\omega_{\rm CT}^{\rm asymp}(R)$ has been calculated with the value $K=0.014$ eV for the parameter $K$ in (9).

Figure 2 shows the qualitatively different behavior of the TDDFT (SAOP–ALDA) and CISD curves $\omega_{\rm CT}(R)$. The latter is the curve with the minimum at $R\approx 2.0$ Å. $\omega_{\rm CT}^{\rm CISD}(R)$ decreases sharply from $\omega_{\rm CT}^{\rm CISD}(R=1\text{ Å})=25.19$ eV to the minimal value $\omega_{\rm CT}^{\rm CISD}(R=2.0\text{ Å})=19.14$ eV and then it increases gradually to 23.74 eV at $R=10$ Å. Contrary to this, the curve $\omega_{\rm CT}^{\rm SAOP-ALDA}(R)$ demonstrates clearly a large underestimation at large $R$ with standard TDDFT of the CT excitation energy, as discussed in the preceding sections.

$\omega_{CT}^{SAOP-ALDA}(R)$ decreases monotonically with $R$ (see Fig. 2) and it resembles $\omega_{CT}^{CISD}(R)$ only in the region $R=1-1.5$ Å, where there is a sizable He–Be interatomic interaction. Beyond this region, $\omega_{CT}^{SAOP-ALDA}(R)$ approaches rapidly the SAOP zero-order asymptotic value $\omega_{CT}^{SAOP(0)}=16.08$ eV. This means that, in accordance with the analysis of the preceding section, the standard ALDA $f_{xc}$ in (8) does not contribute to $\omega_{CT}^{SAOP-ALDA}$ at larger $R$. Unfortunately, $\omega_{CT}^{SAOP(0)}=\varepsilon_{2p}^{SAOP}(\mathrm{Be})-\varepsilon_{1s}^{SAOP}(\mathrm{He})=16.08$ eV is substantially lower than the accurate KS asymptotical value of 18.64 eV, due mostly to failure of the SAOP potential to reproduce for the orbital energy of the $1s$ He AO the required value $-I_{\mathrm{He}}$. The He $1s$ AO is a case for which SAOP performs exceptionally poorly, which may be related to the fact that this orbital energy is substantially lower than typical energies of outer valence orbitals, for which SAOP performs fairly well.[20]

The curve $\omega_{CT}^{asymp}(R)$ is calculated with the asymptotically corrected $f_{xc}^{asymp}$ and the accurate KS orbital energies for $\varepsilon_{2p}(\mathrm{Be})-\varepsilon_{1s}(\mathrm{He})$. In contrast to $\omega_{CT}^{SAOP-ALDA}(R)$ it is close to $\omega_{CT}^{CISD}(R)$ in the whole range of $R=3-10$ Å. In other words, both the CISD calculations and the KS-asymp calculations, employing KS orbital energies and the $f_{xc}^{asymp}$ of (9), reproduce very well the correct Coulombic behavior of $\omega_{CT}(R)$, which originates from the diminishing stabilization $-1/R$ of the transferred electron by the remote hole. Then, an adequate TDDFT description of CT excitations is obtained with the combination of the proper TDDFT curve with the adiabatic LDA approximation for the kernel at $R=1-1.5$ Å and $\omega_{CT}^{asymp}(R)$ at $R=3-10$ Å. The implementation of this combined TDDFT approach requires a proper interpolation between the ALDA xc kernel for compact systems and the present $f_{xc}^{asymp}$ for weakly interacting fragments. It can be achieved with further refinement of the corresponding switching function, which is represented with the exponential function in (9) with the parameter $K$. This refinement, together with exploration of alternative switching functions, will be presented in later work.

## V. CONCLUSIONS

This paper addresses the problem of long-range CT excitation energies $\omega_{CT}$, which are systematically underestimated in the standard TDDFT. It is a fundamental feature of the KS theory that there is in this case a leading correction to $\omega_{CT}^{TDDFT(0)}=\varepsilon_a-\varepsilon_d$, viz. the essentially positive difference $\Delta^A=\varepsilon_a^- -\varepsilon_a$ between the energy $\varepsilon_a^-$ of the ''extra'' electron in the HOMO $\phi_a$ of the anionic acceptor fragment $A^-$ and the energy $\varepsilon_a$ of the ''excited'' electron in the LUMO of the neutral $A$. In TDDFT this correction $\Delta^A$ to $\omega_{CT}^{TDDFT(0)}$ should emerge from a divergent [at $R\to\infty$ and $\phi_d(\mathbf{r})\phi_a(\mathbf{r})\to 0$] xc kernel $f_{xc}$ and this feature as well as the stabilization of the excited electron with the remote hole is reproduced with the function $f_{xc}^{asymp}$ of (9).

The importance of the $f_{xc}^{asymp}$ correction is demonstrated with the calculation of $\omega_{CT}(R)$ for the prototype diatomic system HeBe at various separations $R$(He–Be). While the TDDFT $\omega_{CT}^{SAOP-ALDA}$ roughly resembles the benchmark CISD curve $\omega_{CT}^{CISD}(R)$ in the region $R=1-1.5$ Å where a sizable interatomic interaction exists between He and Be, but fails badly at longer distances, the curve $\omega_{CT}^{KS\text{-}asymp}(R)$ goes close to $\omega_{CT}^{CISD}(R)$ for long-range CT at $R=3-10$ Å. Then, the adequate rigorous TDDFT approach should interpolate between the adiabatic LDA/GGA xc kernel for excitations in compact systems and the present $f_{xc}^{asymp}$ for weakly interacting fragments. Our results highlight once more the importance of using an approximation for the KS xc potential, which would reproduce fairly well the orbital energies of the accurate KS solution. Both at short and at long distance the zero-order TDDFT contribution of just the orbital energy difference is the leading term in the excitation energy. In the particular case of HeBe, the SAOP potential, which is usually reasonable for valence orbital energies, proved to be less satisfactory due to a too high (not negative enough) He $1s$ orbital energy. Because of the well-known much larger upshift of the orbital levels with the LDA/GGA potentials, one can expect an even larger downward shift for the asymptotic LDA/GGA–ALDA type of curves.

The correction of the $f_{xc}^{asymp}$ type should be applied in the general case of an excitation, which involves weakly interacting fragments with KS orbitals localized to a large extent on the fragments. It has been noted[21] that the anomalously low excitation energy sometimes observed in TDDFT calculations on transition-metal complexes,[22] seems to be related to exactly this type of charge-transfer between spatially separated ligands, and might therefore find a natural explanation in the asymptotic error of the ALDA $f_{xc}$, and hopefully be remedied with the asymptotic correction proposed in this work. In practice, the asymptotical correction (9) should be added only to the diagonal elements $K_{ib,ib}$ of the coupling matrix (3). This suggests to consider the following simple approximate interpolation expression for the coupling matrix

$$K_{ib,jc}=K_{ib,jc}^{ALDA}+\delta_{ij}\delta_{bc}\exp(-S_{ii,bb}/S)^2 \times\left[-K_{ib,ib}^{ALDA}+\Delta^A-\frac{1}{R_{ib}}+\frac{(\Delta^A-1/R_{ib})^2}{2(\varepsilon_b-\varepsilon_i)}\right]. \quad (12)$$

In (12) $K_{ib,jc}^{ALDA}$ is the coupling matrix (3) with the standard LDA/GGA ALDA $f_{xc}$ and with the interelectron interaction operator $1/|\mathbf{r}_1-\mathbf{r}_2|$. $S_{ii,bb}$ is the overlap integral between the orbital densities

$$S_{ii,bb}=\int \phi_i^2(\mathbf{r}_1)\phi_b^2(\mathbf{r}_1)d\mathbf{r}_1, \quad (13)$$

and $R_{ib}$ is the ''average distance'' between these densities,

$$R_{ib}=\sqrt{X_{ib}^2+Y_{ib}^2+Z_{ib}^2}, \quad (14)$$

$$X_{ib}=\int [\phi_i^2(\mathbf{r}_1)-\phi_b^2(\mathbf{r}_1)]x\,d\mathbf{r}_1, \quad (15)$$

with analogous expressions for $Y_{ib}$ and $Z_{ib}$. The second term on the right-hand side of (12) represents the CT correction to the diagonal elements $K_{ib,ib}$, which (in the case of a sufficiently small parameter $S$) is switched on whenever the overlap integral (13) becomes small. The quantity $\Delta^A$ could be obtained from a separate calculation on the anionic fragment $A^-$, or approximated from (7), and $R_{ib}$ plays the role of the integral $K_{dd,aa}^{Coul}$ of (9), so that (12) does not require

calculation of any two-electron integral. Further implementation and testing of the CT-corrected coupling matrix (12) is required.

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